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(71) Applicant (for all designated States except US): STFI, SKOGSINDUSTRINS TEKNISKA FORSKNINGSSINSTITUT AB [SE/SE]; Box 5604, S-114 86 Stockholm (SE).

(72) Inventor; and

(75) Inventor/Applicant (for US only): LINDSTRÖM, Tom [SE/SE]; Organistgränd 8, S-192 72 Sollentuna (SE).

(74) Agents: ZACCO SWEDEN AB et al.; P.O. Box 23101, S-104 35 Stockholm (SE).

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(54) Title: METHOD FOR SIZING OF PAPER OR PAPERBOARD.

(57) **Abstract:** The present invention provides, according to a first aspect, a method for internal sizing of paper or paperboard wherein CMC modified cellulose fibres are treated with a synthetic sizing agent, in the presence of an electrolyte whereby the conductivity of the suspension is at least 1.0 mS/cm. The present invention also provides, according to a second aspect, paper or paperboard obtainable by the above method. According to a third aspect of the invention use of paper or paper board according to the second aspect of the invention for the manufacture of liquid board, communication paper, packaging paper, liner or board is provided.

Method for sizing of paper or paperboard

This invention concerns the technical field of paper manufacturing, in particular a method for sizing of paper or paperboard using chemically modified pulps.

5 **Background**

Paper and paperboard are sized (hydrophobated) using different kinds of sizing (hydrophobing) agents. The most common sizing agents are of a rosin type or of the type synthetic sizing agents such as alkyl and alkenyl succinic acid anhydride (hereafter referred to as ASA) or alkyl ketene dimer (hereinafter referred to as AKD). The present invention relates to sizing of paper or 10 paperboard using synthetic sizing agents.

Some technical applications, such as sizing of liquid board, are particularly demanding. For this latter application AKD is especially used, but AKD combined with rosin-based sizing agents are also widely used. It is well known from literature that the sizing operation is not particularly efficient in comparison with what would theoretically be possible to achieve. This depends on a number of 15 factors, in the following exemplified on AKD dispersions but could be valid generally.

First of all, the direct retention of the sizing agent must be high. This depends on that the dispersion is hydrolysed when it is circulated in the process water (this is of course not valid for rosin dispersions – reactive sizing agents only) but also that it agglomerates (e.g. depending on bad dispersion quality) and thus will have a poorer distribution on the fibre surfaces. The distribution 20 ought to be less favourable when using powerful flocculants.

The second important factor is thus that the dispersion particles must be well distributed on the fibre surfaces so that an even distribution of the dispersion particles is obtained, which then are spread over the fibre surfaces to form a molecular film when in contact with air during the drying of the paper. When the AKD has spread over the fibre surfaces, the AKD will subsequently react with 25 the hydroxyl groups on the fibres.

Thirdly, the chemical conditions must be such that the largest part possible of the sizing agent reacts during the drying of the paper. AKD reacts with the hydroxyl groups of the cellulose fibres in a nucleophilic ring-opening reaction, whereupon a covalently bound beta-ketoester is formed. The hydrolysis product (a ketone) is not an efficient sizing (hydrophobation) agent. The reaction is often 30 optimised through the addition of catalysts. The most common catalyst is hydrogen carbonate salt e.g. NaHCO_3 , but also primary, secondary or tertiary amines, which are efficient catalysts (accelerators), are used.

In order to improve retention of synthetic sizing agents, such as AKD, during production of paper and paperboard, different kinds of retention agents are used. These retention agents, though, 35 retain the synthetic sizing agent dispersion but at the same time the retention agent agglomerates the synthetic sizing agent particles, such as AKD, wherefore the results often are far from optimum. Thus,

there is a considerable amount of synthetic sizing agent, which is only wasted. At the same time a poor distribution is achieved. Another problem is that high concentrations of dissolved and colloidal substances interfere with synthetic sizing agents, such as AKD, in closed process water systems. As the dispersion particles are net positively charged and the fibres negatively charged, it is 5 understandable that electrolytes decrease the attraction between the differently charged particles.

Summary of the invention

The present invention solves the above problems by providing, according to a first aspect, a method for internal sizing of paper or paperboard, wherein CMC modified cellulose fibres are treated 10 with a synthetic sizing agent, in the presence of an electrolyte, wherein the conductivity of the suspension is at least 1.0 mS/cm.

The present invention also provides, according to a second aspect, paper or paperboard obtainable by the above method. According to a third aspect of the invention, use of paper or paper 15 board according to the second aspect of the invention for the manufacture of liquid board, communication paper, packaging paper, liner or board is provided.

Detailed description of the invention

It is intended throughout the present description that the expression "CMC modified cellulose fibres" embraces any method whereby cellulose fibres are modified by using CMC. Preferably, the 20 method for modifying cellulose-based material using CMC described in WO 01/21890 is used in the present invention. The method described in WO 01/21890 relates in more detail to a method whereby cellulose fibres are treated for at least 5 minutes with an aqueous solution of CMC or a derivative of CMC containing electrolyte, whereby the temperature during the treatment is at least 100 °C and at least one of the following conditions applies:

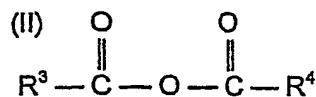
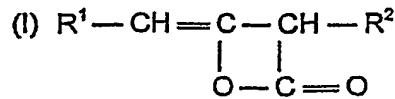
25 A) The pH of the aqueous solution during the treatment lies in the interval of approximately 1.5 - 4.5; or
B) The pH of the aqueous solution during the treatment is higher than approximately 11; or
C) The concentration of the electrolyte in the aqueous solution lies in the interval of approximately 0.001 - 0.5 M if the electrolyte has monovalent cations, or in the range approximately 0.0002 - 0.25 if 30 the electrolyte has divalent cations. It is preferable if condition C applies together with either condition A or condition B. Another method for modifying cellulose fibres with a cellulose derivative such as CMC is described in the published international patent application WO 99/57370. This method was performed at a pH of between 6 - 13 and a temperature of up to 100 °C, preferably in the approximate range 20 - 80 °C. It is intended throughout the present description that the expression 35 "CMC", embraces in addition to carboxymethylcellulose, various derivatives thereof, such as amphoteric CMC, that may e.g. be cationized. A preferred molar degree of substitution (D.S.) may be

approximately 0.3 - 1.3 and a preferred viscosity may approximately be 25 - 8,000 mPa at a concentration of 4%. A higher viscosity may be preferred, since it has become clear that the irreversibility of the adsorption is higher for higher molecular weights. A preferred concentration of CMC may approximately be 0.02 - 4 % w/w, calculated on the dry weight of the fibre material. A 5 more preferred concentration may be approximately 0.04 - 2 % w/w, and the most preferred concentration of additive may approximately be 0.08 - 1% w/w.

It is intended throughout the present description that the expression "electrolyte" embraces one or more electrolytes or mixtures thereof. Examples of electrolytes are given further below.

The cellulose fibres that may be used with the present invention include all types of wood-based fibres, such as bleached, half-bleached and unbleached sulphite, sulphate and soda pulps, together with unbleached, half-bleached and bleached mechanical, thermo-mechanical, chemo-mechanical and chemo-thermo-mechanical pulps, and mixtures of these. Both new fibres and recycled fibres can be used with the present invention, as can mixtures of these. Pulps from both softwood and hardwood trees can be used, as can mixtures of such pulps. Pulps that are not based on wood, such as 10 cotton linters, regenerated cellulose, kenaf and grass fibres may also be used with the present invention.

It is intended throughout the present description that the expression "synthetic sizing agent" embraces any synthetic cellulose-reactive sizing agent such as an agent selected from hydrophobic ketene dimers, (e.g. AKD), ketene multimers, acid anhydrides (e.g. ASA), organic isocyanates, 20 carbamoyl chloride, and mixtures thereof, preferably ketene dimers and acid anhydrides, most preferably ketene dimers. Suitable ketene dimers have the general formula (I) below, wherein R¹ and R² represent saturated or unsaturated hydrocarbon groups, usually saturated hydrocarbons, the hydrocarbon groups suitably having from 8 to 36 carbon atoms, usually being straight or branched chain alkyl groups having 12 to 20 carbon atoms, such as hexadecyl and octadecyl groups. The ketene dimers may be liquid at ambient temperature, i.e. at 25 °C, suitably at 20 °C. Commonly, acid 25 anhydrides can be characterized by the general formula (II) below, wherein R³ and R⁴ can be identical or different and represent saturated or unsaturated hydrocarbon groups suitably containing from 8 to 30 carbon atoms, or R³ and R⁴ together with the-C-O-C-moiety can form a 5 to 6 membered ring, optionally being further substituted with hydrocarbon groups containing up to 30 carbon atoms. 30 Examples of acid anhydrides which are used commercially include alkyl and alkenyl succinic anhydrides and particularly isooctadecenyl succinic anhydride.



Suitable ketene dimers, acid anhydrides and organic isocyanates include the compounds disclosed in U. S. Pat. No. 4,522,686, which is hereby incorporated herein by reference. Examples of suitable carbamoyl chlorides include those disclosed in U. S. Pat. No. 3,887,427, which is also incorporated herein by reference.

5 The amount of sizing agent added to the aqueous suspension containing CMC modified cellulose fibres can be from 0.01 to 5 % by weight, suitably from 0.02 to 1.0 % by weight, based on dry weight of cellulose fibres and optional fillers, where the dosage is dependent on the quality of the pulp or paper to be sized, the sizing agent and the level of sizing. The pulp may have a consistency ranging from low consistency to high consistency.

10 It is intended throughout the present description that the expression "AKD" embraces in addition to alkyl ketene dimer, various derivatives thereof. When manufacturing AKD dispersions/emulsions then the reactive wax may be heated to temperatures above 80°C at a low pH (3-4) whereupon different dispersing agents are added.

15 According to a preferred embodiment of the first aspect of the present invention, the synthetic sizing agent is comprised in a sizing dispersion, comprising at least one cationic component and/or at least one anionic component. Preferably the cationic component is cationic starch. Preferably the anionic component is a lignin derivative such as lignosulphonic acid and/or condensation product of formalehyde and naphtalenesulphonic acids. The most common dispersing agent in commercial preparations is cationic starch combined with lignosulphonic acid or naphtalenesulphonic acid that 20 were used in the examples of the present description. This results in amphoteric AKD-dispersions (sizing dispersions) that may be deposited on anionic fibre surfaces.

25 The stock, i.e. the pulp treated with CMC (or a derivative thereof), which is acting as raw material, comprising electrolyte may further comprise said electrolyte naturally or the electrolyte may be added to the stock. Normally the stock already comprises an amount of electrolytes that are enough for performing the method according to the present invention and thus obtain the advantageous effects of the present invention. Usually, the conductivity of the stock is at least 1.0 mS/cm, suitably at least 3.5 mS/cm. The conductivity levels may also preferably be above 5.0 mS/cm and even above 7.5 mS/cm. Conductivity can be measured by standard equipment such as, for example a WTW LF 539 instrument supplied by Christian Berner. The values referred to above are suitably determined by 30 measuring the conductivity of the cellulosic suspension that is fed into or present in the headbox of the paper machine or, alternatively, by measuring the conductivity of white water obtained by dewatering the suspension. The conductivity levels are preferably a result of relatively high contents of salts (electrolytes), where the various salts can be based on mono-, di-and multivalent cations like alkali metals, e. g. Na^+ and K^+ , alkaline earths, e. g. Ca^{2+} and Mg^{2+} , aluminium ions, e. g. Al^{3+} , Al(OH)^{2+} and polyaluminium ions, and mono-, di-and multivalent anions like halides, e. g., Cl^- , sulfates, e. g. SO_4^{2-} carbonates, e. g. CO_3^{2-} and HCO_3^- , silicates and lower organic acids or mixtures thereof.

The invention may be particularly useful in the manufacture of paper from stocks having high contents of salts of di-and multivalent cations. The salts can be derived from the cellulosic fibres and fillers used to form the stock, in particular in integrated mills where a concentrated aqueous fibre suspension from the pulp mill normally is mixed with water to form a dilute suspension suitable for 5 paper manufacture in the paper mill. The salt may also be derived from various additives introduced into the stock, from the fresh water supplied to the process, or be added deliberately, etc. Further, the content of salts is usually higher in processes where white water is extensively re-circulated, which may lead to considerable accumulation of salts in the water circulating in the process.

According to a further preferred embodiment of the first aspect of the present invention the 10 electrolyte is selected from the group consisting of the following ions: Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} and HCO_3^- .

According to a further preferred embodiment of the first aspect of the present invention the concentration of the electrolyte lies above 0.0001 M, preferably in the interval of approximately 0.0002- 0.1 M, most preferred 0.001 - 0.02 M.

15 According to a further preferred embodiment of the first aspect of the present invention a retention agent is additionally used in the method of the first aspect. Any cationic retention agent or retention system (dual and three-component system commonly used in paper manufacture) containing at least one cationic component may be used. The retention agent may e.g. be selected from the group consisting of cationic starches (based on e.g. wheat, maize, potato, tapioca, rice, waxy 20 maize) and gums (such as guar, tamarind, locust bean gums), cationic cellulose derivatives (e.g. chitosan), vinyl addition polymers like acrylate- and acrylamide copolymers with cationic vinyl monomers (e.g. N,N,N-trimethylaminoethyl acrylate, N,N,N-trimethylaminopropylmethacrylamide, 3-acrylamide-3-methylbutyltrimethylammoniumchloride etc), step-grown polymers such as 25 polyamines (polymers of halohydrin type e.g. epichlorohydrins polymerized with dimethylamine and smaller quantities of ammonia and/or primary amines), polyamidamines (e.g. dicarboxylic acids e.g., adipic acid condensed with amines such as etylenediamine, hexamethyldiamine, diethylenetriamine 30 grafted with epichlorohydrine and/or ethyleneimine), polydiallyldimethylammoniumchloride (and copolymers with acrylamide), polacrylamides grafted with dimethyl-amine and formaldehyde (Mannich-type PAM), polyacrylates grafted with ethylenenimine etc. A cationic polyacrylamide, such as Percol 292 may e.g. be used. The retention agent may further be comprised of a system of retention 35 agents. The cationic polymer may conveniently be combined with an anionic/amphoteric component such as anionic silica sols, sodium montmorillonites or anionic polyacrylamides (hydrolysed polyacrylamide or co-polymers between acrylic acid and acrylamide) and various aluminium salts (aluminium sulfate, polyaluminium chlorides or sulfates) used under neutral or alkaline conditions (pH above 6.0). In addition, such dual component systems may be complemented by other non-ionic, anionic, amphoteric or cationic polyelectrolytes to yield various multi-component systems.

The method according to the present invention may further be used in papermaking processes where white water is extensively re-circulated (recycled), i. e. with a high degree of white water closure, for example, where from 0 to 30 tons of fresh water are used per ton of dry paper produced, usually less than 20, suitably less than 15, preferably less than 10 and notably less than 5 tons of fresh water per ton of paper. Re-circulation of white water obtained in the process suitably comprises mixing the white water with cellulosic fibres and/or optional fillers to form a suspension (stock) to be sized; preferably it comprises mixing the white water with a suspension containing cellulosic fibres, and optional fillers, before the suspension enters the forming wire.

The paper or paper board obtainable by the method according to the first aspect of the present invention may be used for the manufacture of liquid board, various communication papers, such as newsprint grades, supercalendered SC-grades and coated communication papers such as light weight coated papers (LWC), MWC (medium weight coated) and HWC (high weight coated) and various packaging papers, kraft- and test liners and various board grades from recycled boards, folding boxboards and solid bleached boards. The invention is not only limited to these grades but to all grades where it is desirable to use a synthetic sizing agent.

The invention is thus based upon the discovery that when using fibres modified with CMC and sized with a synthetic sizing agent in the presence of an electrolyte a good distribution and a high retention of the synthetic sizing agent is obtained. The effect is surprising as addition of electrolytes normally results in a worse retention, as theoretically, a lower retention would be expected when increasing the electrolyte addition. This is also the case when using fibres, which are not modified with CMC. The effect is especially interesting in many technical systems as it is normally difficult to retain synthetic sizing agent in systems with high electrolyte concentrations e.g. in closed systems.

An explanation to the unexpected positive effect, which the present inventor is not bound to in any way, of the present invention could be that the distribution of the deposited synthetic sizing agent particles on the pulp is better with the present method according to the present invention. When a cationic polyelectrolyte is used then the dispersion is agglomerated by the flocculant whilst the presence of electrolyte apparently achieves a more uniform distribution of the synthetic sizing agent particles on the fibre surfaces as the amount of reacted synthetic sizing agent is essentially independent of electrolyte concentration and retention aid addition.

Preferred features of each aspect of the invention are as for each of the other aspects mutatis mutandis. The prior art documents mentioned herein are incorporated to the fullest extent permitted by law. The invention is further described in the following examples in conjunction with the appended figures, which do not limit the scope of the invention in any way. Embodiments of the present invention are described in more detail with the aid of examples of embodiments, the only purpose of which is to illustrate the invention and are in no way intended to limit its extent.

Short description of the figures

Fig 1 shows the retention of AKD to an untreated pulp as a function of electrolyte concentration.

5 Fig. 2 shows that the degree of sizing decreases quickly at electrolyte concentrations corresponding to 0.01 M.

Fig. 3 shows the effects of electrolyte concentration on the retention of AKD to the same pulp treated with CMC.

10 Fig. 4 shows the corresponding Cobb-60-results and these show as expected that the degree of sizing is very much increased in the presence of an electrolyte.

Fig. 5 shows that is possible to retain the AKD dispersion with a cationic polyelectrolyte (in this case a cationic polyacrylamide, Percol 292) in the presence of an electrolyte, in this case 0.01 M CaCl₂.

15 Fig 6. shows that 0.6 mg/g AKD is necessary in order to achieve sizing with the reference pulp when using a retentation agent. If using the CMC-treated fibres instead in the absence of electrolyte then a similar amount of AKD is consumed as in the reference case. It is when using the CMC-treated fibres in the presence of an electrolyte the technically interesting effects with an approximately halved consumption of AKD (0.3 mg/g) appear.

20

Examples**Example 1:****Preparation of fibres with CMC (see WO 01/21890)**

CMC-treatment was performed in the following manner: To the commercial long-fibred, softwood pulp (Husum MoDoKraft GT, 2.5% conc.) 10 mg/g Finnfix WRH, 10 mM NaHCO₃ (buffer) 25 and 0.05 M CaCl₂ was added, whereupon the pH was adjusted to pH=8 with NaOH, whereupon the pulp dispersion was heated in a pressurized vessel to 120°C during 2 hours. Thereafter, the pulp was washed with de-ionised water, acidified with HCl (pH=2) and buffered with 1mM NaHCO₃, whereupon the pH was adjusted to pH=9 with NaOH. The pulp, now in its Na-form, was leached during 2 hours, whereupon it was washed with de-ionised water. Then the pulp was treated with 30 MgCl₂ and CaCl₂, respectively, in excess (0.05 M solution) and thereupon with de-ionised water in order to get the desirable ion form before the experiments.

Preparation of dispersions with C-14 AKD

In the experiments a C-14 labelled AKD dispersion was used in order to measure the retention 35 of the dispersion to the paper. The AKD dispersion was made in the laboratory of STFI according to a recipe obtained from EKA Chemicals with lignosulphonic acid and cationic starch as a base i.e. the

cationic component and the anionic component, respectively. Such AKD dispersions that were used are also disclosed in US 4,861,376 and US 6,001,166; both hereby incorporated by reference. See also WO02/12622: hereby incorporated by reference. In US 4,861,376, the cationic starch stabilizer is any water soluble starch carrying sufficient cationic amino groups to render the starch positively charged in solution. The preferred starches in US 4,861,376 are cationic waxy maize starches of low to moderate viscosity (Brookfield viscosity of from about 50 to about 200 cst), with either tertiary or quaternary amino groups as the source of the charge. Starches to use are tertiary amine modified waxy maize having a Brookfield viscosity of from about 50 to about 80 cst, such as TM Amaizo 2187 (sold by American Maize-Products Co.) or a quaternary amine modified waxy maize of the same viscosity, such as TM Stalok 140 (sold by A. E. Staley Manufacturing Co.). The starch can be present in an amount of from about 10 to about 30% by weight dimer. Preferably the starch is present in an amount from about 15 to about 25% by weight and most preferably from about 18 to about 22% by weight. The sulfonate stabilizers are various salts of lignin sulfonic acid and the condensation product of formaldehyde and various salts of naphthalene sulfonic acid and mixtures thereof.

In US 6,001,166 the cationic starches having amylopectin contents of at least 95% are present to an extent of from 0.5 to 5% by weight, preferably from 1 to 3% by weight, in the aqueous alkyldiketene dispersion. The finely divided, aqueous alkyldiketene dispersions are usually prepared by first converting the starches containing at least 95% of amylopectin into a water-soluble form. This can be achieved, for example, by means of oxidative or hydrolytic degradation in the presence of acids or by simply heating the cationic starches. The digestion of the starch is preferably carried out in a Jet digester at from 100 to 150° C. In the aqueous solution of the cationic starch having a minimum amylopectin content of at least 95% by weight obtainable in this way, there is then dispersed at least one C₁₄ -C₂₂ -alkyldiketene, preferably in the presence of dispersants at above 70 ° C., e.g. in the range from 70 to 85° C. However, if desired, the alkyldiketenes can also be dispersed in the presence of at least one dispersant. To obtain the dispersions the other dispersant is then added and the dispersion is homogenized if necessary. However, the dispersants can also be added to the dispersion obtained after dispersing the alkyldiketene in the above described aqueous solution of a cationic starch, with the mixture then usually being further subjected to a high shear rate, e.g. in a homogenizer at pressures of up to 1000 bar. The alkyldiketene dispersion is then cooled so that the alkyldiketenes are present in solid form. This gives finely divided aqueous alkyldiketene dispersions having a mean particle diameter of, for example, from 0.5 to 2.5 µm, preferably from 0.8 to 1.5 µm. Suitable dispersants are ligninsulfonic acid, condensates of formaldehyde and naphthalenesulfonic acids, polymers containing styrenesulfonic acid groups, for example sulfonated polystyrenes, or the alkali metal and/or ammonium salts of said compounds containing sulfonic acid groups. They are present in the aqueous alkyldiketene dispersion in amounts of from 0.05 to 1.0% by weight, preferably from 0.01 to 0.5% by weight. The aqueous alkyldiketene dispersions may also contain as an additional

dispersant (an additive) from 0.05 to 1.5% by weight of sulfuric monoesters of alcohols having at least 10 carbon atoms, phosphoric monoesters or diesters of alcohols having at least 10 carbon atoms, sulfuric monoesters of alkoxylated alcohols having at least 10 carbon atoms, phosphoric monoesters or diesters of alkoxylated alcohols having at least 10 carbon atoms, C_{12} - C_{30} -alkylsulfonic acids, salts and mixtures of said compounds. The sulfuric monoesters are preferably derived from alcohols having from 12 to 30 carbon atoms or from mixtures of such alcohols. Suitable alcohols for the preparation of sulfuric esters are, for example, lauryl alcohol, palmityl alcohol, stearyl alcohol, behenyl alcohol and the long-chain alcohols obtainable by the so called oxo process. Similar AKD dispersions are also disclosed in US 3,223,544; hereby incorporated by reference.

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Production of handmade sheets

Paper was made in a manually operated sheet former according to the following method: A pulp suspension with untreated (reference) and treated (with Finnfix WRH, CMC) bleached softwood pulp, respectively, was put into a suitable ion form (Na, Ca or Mg) and was dispersed in de-ionized water at a concentration of 2.5 g/l. $NaHCO_3$ (accelerator) was added to a final concentration corresponding to 1 mM. The AKD dispersion was added and the dispersion was mixed during 30 seconds whereupon a retention agent (Percol 292, cationic polyacrylamide) was mixed with the pulp during 30 seconds, whereupon the pulp suspension was diluted in a sheet former with an electrolyte solution so that the final electrolyte concentration was obtained in the manually operated sheet former (1mM $NaHCO_3$ and x mM electrolyte; see results and figures for the explanation of x). Hand made sheets were manufactured with a basis weight of 80 g/m². The sheets were couched, dried in a photo drier at 90 °C during 10 min between 2 fine mesh nylon wires. Thereupon, the sheets were cured at 110°C during 10 min.

25

Testing

After conditioning at 23°C at 50%RH, the Cobb value (60 sec) was measured as a measure of the degree of sizing. The sheets were then incinerated in a so called oxidizer and the free carbon dioxide (C-14) was absorbed in a so called scintillation cocktail whereupon the radioactivity of the sample could be measured with the help of a liquid scintillation counter apparatus and the retention could be calculated from added and retained amount of AKD. The amount of reacted AKD (approx. 40-50%) was also determined, but this amount is practically independent of the concentration of electrolyte in the presence of an accelerator (1mM $NaHCO_3$), wherefore this is not accounted for here.

Results

Fig 1 shows the retention of AKD (in %) to an untreated pulp (S.W. kraft = soft wood kraft) as a function of electrolyte concentration. The retention decreases strongly in the presence of NaCl, CaCl₂ or MgCl₂. From figure 1 it is possible to see that the single pass retention of AKD (without retention agent) quickly decreases to below 10% at electrolyte concentrations over 0.01 M. The surface charge of the fibres was 2.78 μ ekv/g. The AKD dose was 1 mg/g. (acc. = accelerator).

Fig. 2 shows that the degree of sizing decreases quickly at electrolyte concentrations in excess of 0.01 M. The conclusion of this is that it is very difficult to size at high electrolyte concentrations without a retention agent. The surface charge of the fibres was also here 2.78 μ ekv/g. The AKD dose was 1 mg/g.

Fig. 3 shows the effects of electrolyte concentration on the retention of AKD to the same pulp treated with CMC. It can be seen that the retention quickly increases with increased electrolyte concentration and a maximum retention of approximately 70 % at 0.01 M CaCl₂/MgCl₂ is obtained, whereupon the retention decreases. In the case of NaCl, the maximum is displaced towards higher electrolyte concentrations. These results show that in the presence of an electrolyte, it is possible to achieve very high retention values if the pulp has been treated in accordance with the method of the present invention. This result is highly unexpected, as the common theory for retention based upon heterocoagulation between the cationic AKD dispersion particle and the negatively charged fibre, would suggest a unilateral decreasing retention as in Figure 1. (Fibres with a similar surface charge density as the treated fibres do not behave as the results of Fig 3. but as in Figure 1 - curves that show the lack of this synergistic effect). The surface charge of the fibres was 12.2 μ ekv/g. The AKD dose was 1 mg/g. The amount of CMC added during the attachment to the fibres was 10 mg/g.

Fig. 4 shows the corresponding COBB₆₀-results and these results show as expected, that the degree of sizing is very much improved in the presence of an electrolyte. When the Cobb value increases the sizing decreases. During practical paper manufacture, it is common to use a retention agent in order to retain AKD-dispersions and it is additionally possible to, with good effect, retain the AKD dispersion also in the presence of high electrolyte concentrations. The surface charge of the fibres was also here 12.2 μ ekv/g. The AKD dose was 1 mg/g. The CMC added during the attachment to the fibres was 10 mg/g.

Fig. 5 shows that is possible to retain the AKD dispersion with a cationic polyelectrolyte (in this case a cationic polyacrylamide, Percol 292, 0.1 %) addition in the presence of an electrolyte, in this case 0.01 M CaCl₂. As is indicated in figure 5 the CMC treated fibres give a somewhat increased retention than the reference pulp even though the differences are not that large. What is more surprising (see figure 6) is, however, that the consumption of sizing agent in order to obtain a fully sufficient degree of sizing (COBB₆₀ less than 25 g/m²) has been halved.

Fig. 6 shows that 0.6 mg/g AKD is necessary in order to achieve sizing with the reference pulp when using a retention agent. If using the CMC-treated fibres instead in the absence of electrolyte then a similar amount of AKD is consumed as in the reference case. It is when using the CMC-treated fibres in the presence of an electrolyte the technically interesting effects with an approximately halved consumption of AKD (0.3 mg/g) appear.

Various embodiments of the present invention have been described above but a person skilled in the art realizes further minor alterations, which would fall into the scope of the present invention. The breadth and scope of the present invention should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims and their equivalents. For example, any of the above-noted dispersions (stocks) and/or methods can be combined with known methods. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

Claims

1. Method for internal sizing of paper or paperboard, characterised in that CMC modified cellulose fibres are treated with a synthetic sizing agent, in the presence of an electrolyte, 5 wherein the conductivity of the suspension is at least 1.0 mS/cm.

2. Method according to claim 1, characterised in that the synthetic sizing agent is comprised in a sizing dispersion, comprising at least one cationic component and at least one anionic component, preferably the synthetic sizing agent is AKD.

10 3. Method according to claim 1, characterised in that the synthetic sizing agent is added in an amount to the suspension containing CMC modified cellulose fibres from 0.01 to 5 % by weight, preferably from 0.02 to 1.0 % by weight.

15 4. Method according to claim 1, characterised in that the concentration of the electrolyte lies above 0.0001 M, preferably in the interval of approximately 0.0002- 0.1 M, most preferred approximately 0.001 - 0.02 M.

20 5. Method according to claim 1, characterised in that a retention agent is additionally used.

6. Method according to claim 5, characterised in that the retention agent is comprised in a system of retention agents.

25 7. Method according to claim 1, characterised in that the electrolyte is selected from the group consisting of the following ions: Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} and HCO_3^- .

30 8. Method according to claim 1, characterised in that the CMC modified cellulose fibres have been treated with CMC with a concentration of approximately 0.02 - 4 % w/w, preferably approximately 0.04 - 2 % w/w, most preferred approximately 0.08 - 1% w/w.

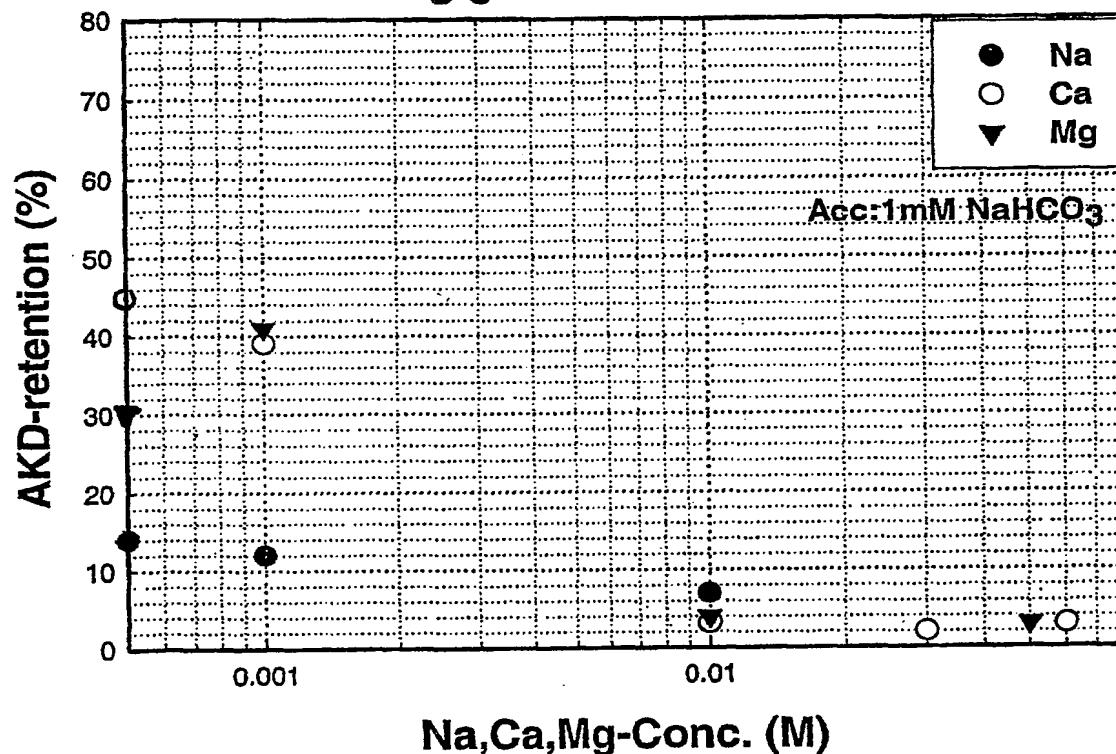
9. Paper or paperboard obtainable by a method according to either of claims 1-8.

35 10. Use of paper or paper board according to claim 8 for the manufacture of liquid board, communication paper, packaging paper, liner or board.

1/6

Fig. 1

S.W. kraft (ref./ surface charge: 2.78 μ ekv/g)
AKD-dos. 1 mg/g



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Fig. 2

S.W.kraft (ref./surface charge : 2.78 μ ekv/g)
AKD-dos.1 mg/g

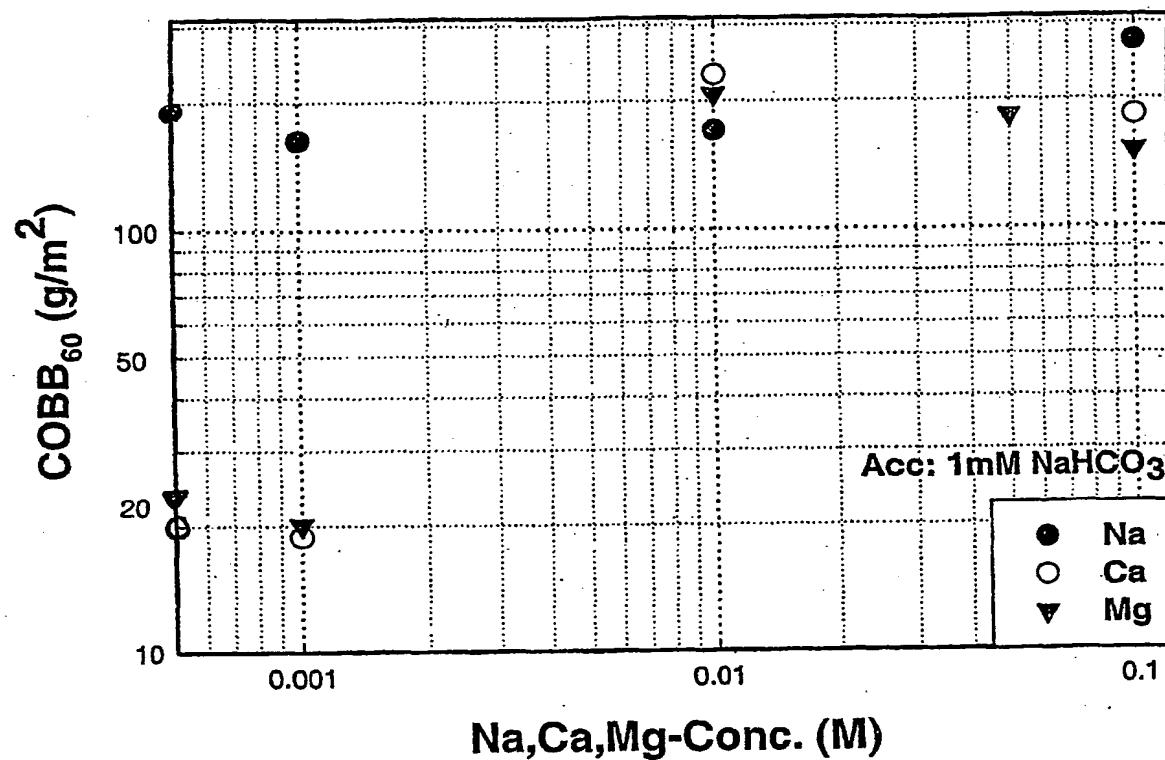


Fig. 3

**S.W. kraft (CMC / 10mg/g /surface charge : 12.2 μ ekv/g)
AKD-dos. 1 mg/g**

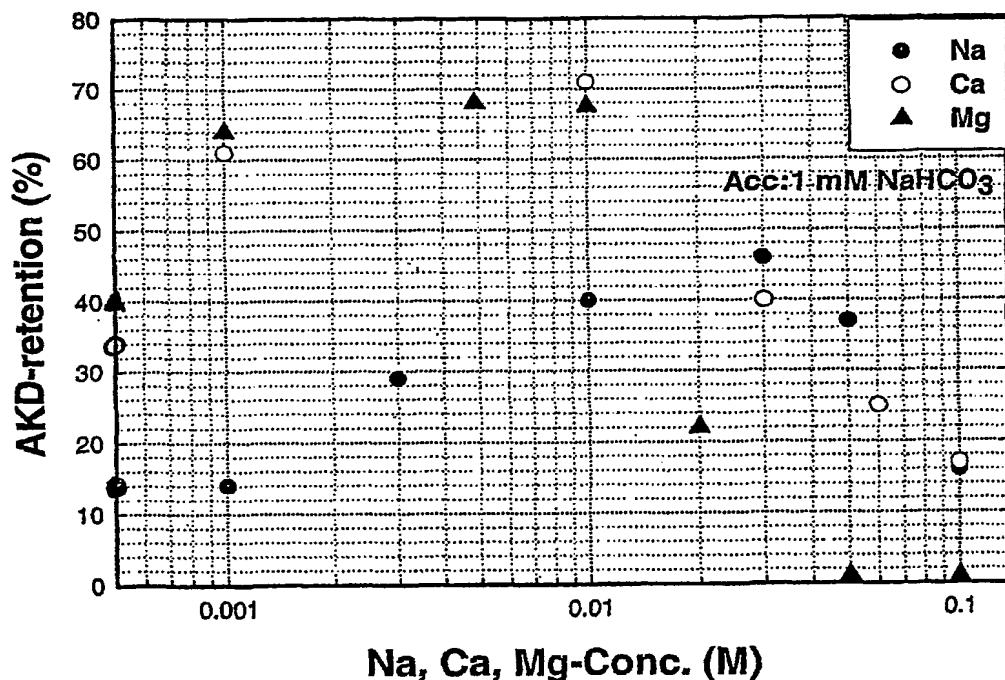


Fig. 4

**S.W. kraft (CMC / 10 mg/g /surface charge: 12.2 μ ekv/g)
AKD-dos 1 mg/g**

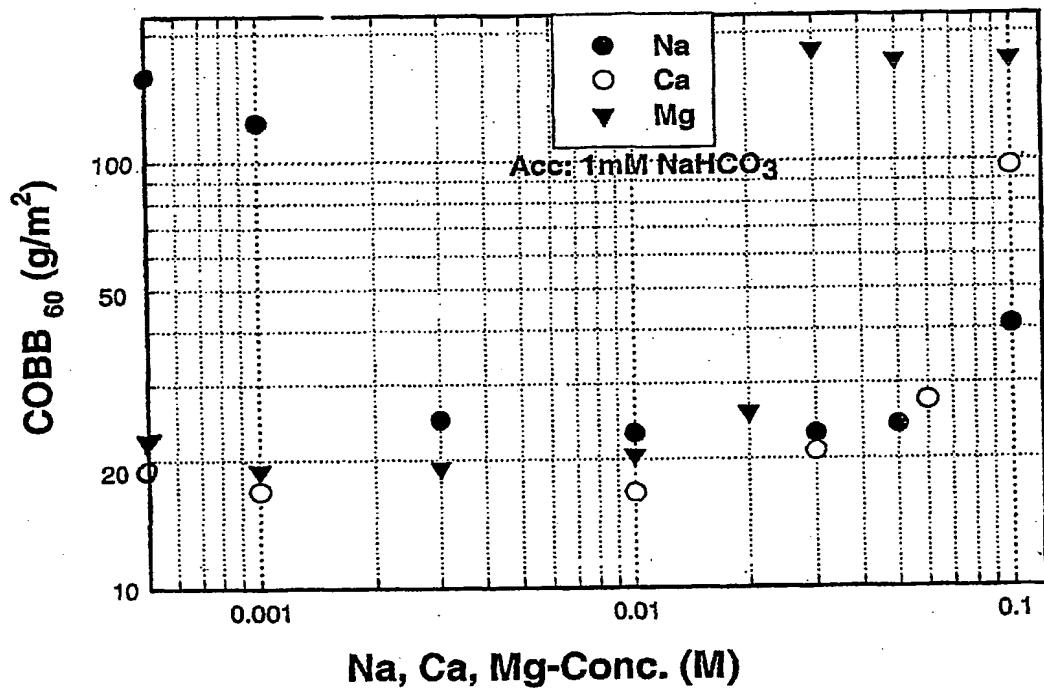


Fig. 5

S.W. kraft (ref./surface charge : 2.78 μ ekv/g)

S.W. kraft (CMC / 5 mg/g / surface charge : 8.93 μ ekv/g)

S.W. kraft (CMC /10 mg/g / surface charge : 12.2 μ ekv/g)

P 292 (0.1%)

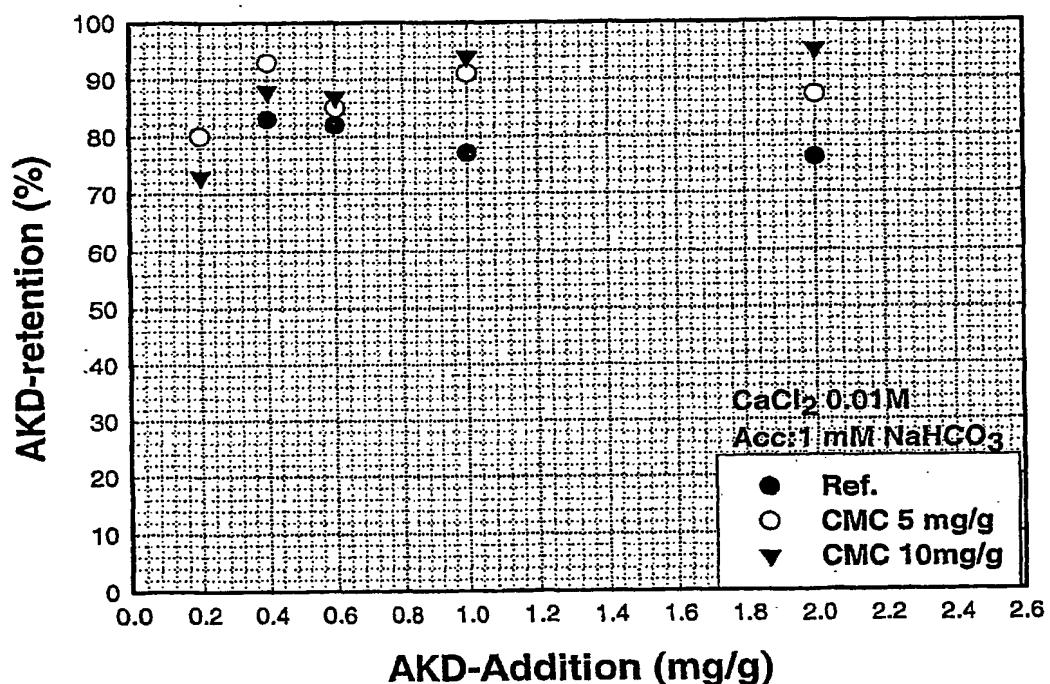
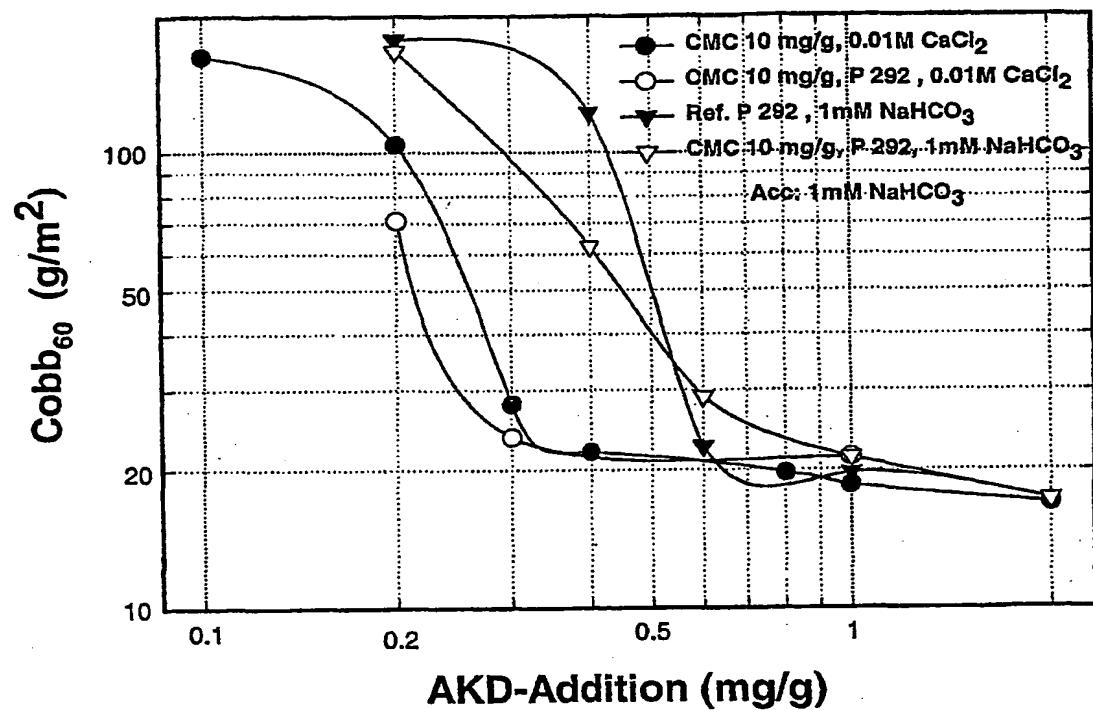


Fig. 6

S.W. kraft (ref./surface charge : 2.78 μ ekv/g)
S.W. kraft (CMC/10 mg/g/ surface charge : 12.2 μ ekv/g)



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/01400

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 21/16, D21C 9/00 // D21H 11/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21C, D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, PAJ, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0723047 A2 (HERCULES INCORPORATED), 24 July 1996 (24.07.96), page 1 - page 2; page 6, line 42 - line 44, abstract --	1-10
A	WO 0121890 A1 (STFI), 29 March 2001 (29.03.01), page 4, line 25 - line 30, abstract --	1-10
A	US 4517285 A (ANTONY I. WOODWARD ET AL), 14 May 1985 (14.05.85), claim 1 --	1-10
A	WO 9833982 A2 (AKZO NOBEL N.V.), 6 August 1998 (06.08.98), page 1, abstract --	1-10

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

2 December 2003

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Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. + 46 8 666 02 86

Authorized officer

Barbro Nilsson/Els
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 03/01400

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

06/09/03

International application No.

PCT/SE 03/01400

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Information on patent family members

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International application No.

PCT/SE 03/01400

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